Studies on Zn (II) ion Adsorption by Rice Husk Digested with Nitric Acid and Sodium Hydroxide

By

Syafiq Effendi Bin Jalis

Dissertation submitted in partial fulfillment of
the requirement for the Bachelor of Engineering (Hons)
(Chemical Engineering)

Universiti Teknologi Petronas,
Bandar Seri Iskandar,
31750 Tronoh,
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

STUDY ON Zn (II) ION ADSORPTION BY RICE HUSK DIGESTED WITH NITRIC ACID AND SODIUM HYDROXIDE

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SYAFIQ EFFENDI BIN JALIS (2628)

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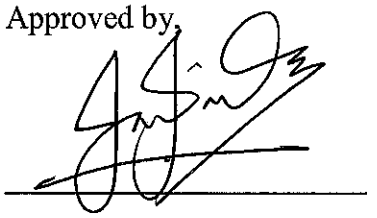
Approved by,



Mr. Mohd. Faisal Taha
Research Supervisor

Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Bandar Seri Iskandar, Tronoh, Perak Darul Ridzuan

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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SYAFIQ EFFENDI BIN JALIS

ABSTRACT

There are two procedures that commonly govern the studies on metal adsorption by rice husk. They are the treatment process of the rice husk and the adsorption process of the metal ion. Raw rice husk will be treated with acidic or basic solution and then pyrolised before it can be used as adsorbent. The treatment process of the rice husk can enhance the surface properties and thus, increase the capability of the rice husk to be used as adsorbent.

In this piece of work, three factors were considered in order to compare the performances of the acid and base treated rice husk. Effect of digestion times, contact time and initial metal ion concentration on the Zn (II) ion adsorption were conducted in this research. The performance of the rice husk as adsorbent was compared by analyzing the percent metal uptake and the adsorption capacity of the rice husk.

As the digestion time increased, the percent metal uptake also increased. For effect of contact time, the percent metal uptake increased as the contact time increased until an optimum time was reached, whereby further increase in the contact time did not change the adsorption rate. The percent metal uptake increased as the initial metal ion concentration increased until an optimum initial metal ion concentration was reached. After the optimum initial metal concentration was reached, further increase in the initial metal concentration resulted in the reduction of the percent metal uptake. Based on these three effect studies, it was found out that the acid treated rice husk was better adsorbent compared to base treated rice husk.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

A number of studies on converting rice husk to activated carbon have been reported [1]. Rice husk is agricultural waste, accounting for about one-fifth of the annual gross rice, 545 million metric tons of the worlds [4]. As the demand using renewable resource for alternatives is rising rapidly with the decrement of irrenewable resource, the studies done on the potential of the rice husk is considered to be very essential and important.

Before it can be used as an adsorbent, a few methods have been identified to treat this rice husk. These treatment processes include the activation of the rice husk. There is no exact method has been proven to produce a high performance adsorbent from rice husk. The previous studies conducted show that the rice husk needs to be digested with acidic or basic solution [1, 2, 3, 4, 6]. However, there are no studies done to compare between these two types of digestion solution on the rice husk. Therefore, the performances of these two types of digested rice husk have been tested, examined and compared in this piece of work.

There are no exact explanations of how the rice husk particles form its binding with the metal ion. However, the formation of the surface complexes is most likely to be related to the predominant silica content of the samples [1]. This is where the digestion process takes place. The digestion process reduces the organic constituents and produced a highly porous cellulose-silica material which has a relatively good adsorptivity in removing Zn (II) without using other activating chemical. In all cases, rice husk is pyrolised in an inert atmosphere (nitrogen or argon) in order to remove volatile matter.

1.2 PROBLEM STATEMENT

Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment. The common toxic metals i.e. Cd, Zn, Ni, and Pb find their way to the water systems i.e. river, dam and sea through waste waters. In order to evaluate the reaction of these heavy metals to the adsorption activities, Zn (II) has been chosen as adsorbate since this cation is commonly found in industrial wastes [1]. The release of large quantities of heavy metals into the natural environment e.g. irrigation of agricultural fields by using sewage, has resulted in a number of environmental problems. Due to their non-biodegradability and persistence, these heavy metals can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health [7].

The interest in the development of the cost-effective methods for the removal and recovery of heavy metal from contaminated waters has greatly increased because of the ecological awareness of the role of metals in the environment [8]. There are lots of chemical methods used to remove this heavy metal from the industrial waste such as precipitation, ion-exchange, membrane separation, and adsorption [3]. Activated carbon is a very efficient solid sorbent in many different applications. However, activated carbon is an expensive process and the need of an alternative low-cost sorbent has encouraged the search for new adsorption process [8]. The major attention has been focused on abundant biomass types generated as a waste by-product of large scale industrial processes and vegetable biomass [8].

Due to the growing concern with environment pollutions, and the need to conserve energy and resources, efforts has been made to burn rice husks under controlled temperature and atmosphere as supplementary cementing material. The results of Feng et. al [4] showed that the treatment of the rice husk with an acid solution for 4 hours produced ash with high surface area. Rice husk is also said to have granular structure, insolubility in water, chemical stability and local availability [8]. Therefore, the need to study on the potential of the rice husk is considered to be very essential and important.

1.3 OBJECTIVES AND SCOPE OF STUDY

In order to complete this project within the time limit and scope given, three objectives have been identified as follows:

i. To compare the performance of acid treated rice husk and base treated rice husk.
ii. To study the effect of digestion time on the rice husk
iii. To study the effect of contact time and initial metal concentration on adsorption activities.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 EFFECT OF DIGESTION TIMES OF BASIC AND ACIDIC ACTIVATION ON ADSOPRTION ACTIVITIES

Not much work has been performed on the digestion or the activation of the rice husk. However, it is believed that the digestion is done to reduce the organic constituents of the rice husk [1]. The digestion produced a highly porous cellulose-silica material which has a relatively good adsorptivity in removing Zn (II) [1]. There is also study reported that the acid treated biomass had enhanced surface properties rather than base treated biomass [6]. The difference in surface properties of acidic and basic treatment could be due to the presence of high affinity ligands in the biomass such as cyano and amino groups on the biomass surface [6].

At high pH (7-8), metal ion may be forced to bind to low affinity ligands such as hydroxyl and carboxyl groups but at low pH (1-3), the binding may occur through high affinity ligands only [6]. This is an indication that the degree of ionization on the biomass surface is pH dependent [6]. This affect the metal ion adsorption activities by the biomass as the overall surface charge in the biomass influences the metal adsorption [6].

2.2 EFFECT OF CONTACT TIME ON ADSORPTION ACTIVITIES

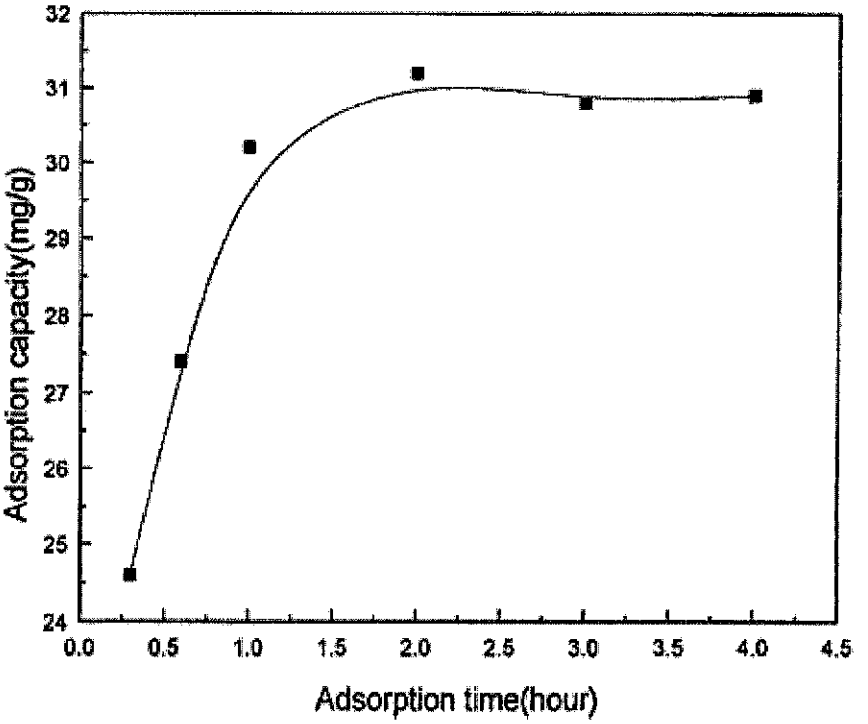

Figure 2.1: Adsorption of Cr (VI) on rice husk based activated carbon as a function of contact time. Conditions—Cr (VI): 39.51 mg l−1; RHC: 0.8 g l−1; temperature: 20 °C; pH: 5.0 [3].

A graph shown above is an example of the effect of contact time to the adsorption activities. The type of metal ion adsorped is also one of the factors that may affect the result of adsorption capacity. Several studies conducted on the contact time effect of rice husk adsorbent to the adsorption of metal ion indicated that as the contact time increased, the metal ion adsorped also increased [2, 3, 8]. It was noted that about after 3 hours of adsorption, the rate of adsorption became constant which means the adsorption process had achieved equilibrium [2, 3, 8]. However, the fast kinetics between the rice husk and the metal depends on the analytical speed and the removal efficiency [8]. Therefore these factors need to be considered and must be made constant as the effect of contact time is studied.

2.3 EFFECT OF INITIAL METAL CONCENTRATION ON ADSORPTION ACTIVITIES

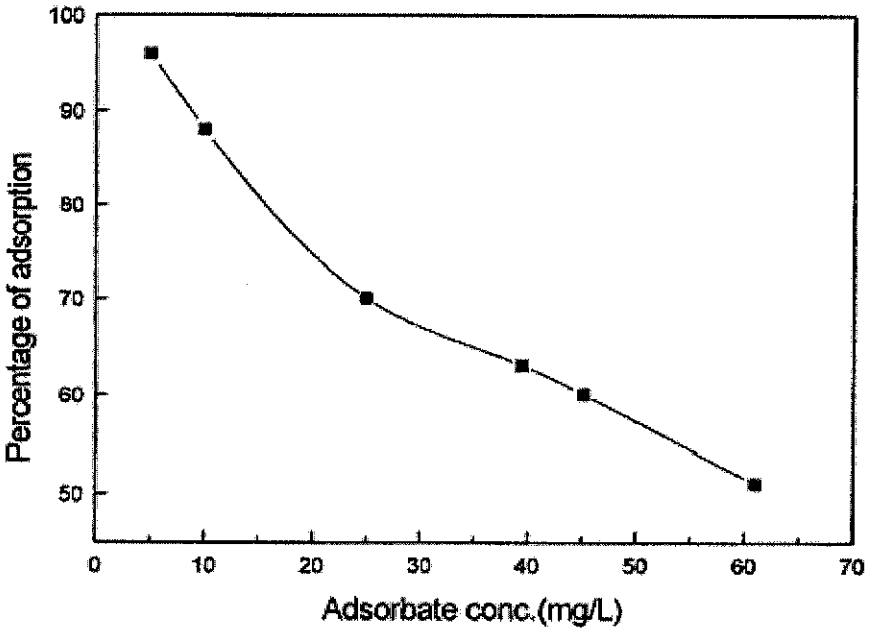

Figure 2.2: Adsorption of Cr (VI) on rice husk based activated carbon as a function of initial Cr (VI) concentration. Conditions—pH: 5.0; RHC: 0.8 g l−1; temperature: 20 ◦C [3].

The above graph is an example of the effect of initial metal concentration of Cr (VI) to the adsorption activities. The type of metal ion adsorped is also one of the factors that may affect the result of adsorption capacity. As the concentration of metal ions increases the metal loading on the adsorbent also increases [5]. With the increase in metal ion concentration, the number of active adsorption sites is not enough to accommodate adsorbate ions [3].

The limit of pore size dimension and electrostatics repulsion between negative charge of adsorbate ions results in the decrease of adsorption percentage [3]. It is agreed that as the metal ion concentration is increased, the metal ion sorption also increased until an optimum concentration is reached. At this optimum metal ion concentration, an additional increase of initial metal concentration will not change the capacity of the metal sorption by rice husk [8]. However, the sorption efficiency is reduced with increasing metal ion concentration in the solution, thus indicating saturated solution is reached [3, 5, 8].

2.4 EFFECT OF pH ON ADSORTION ACTIVITIES

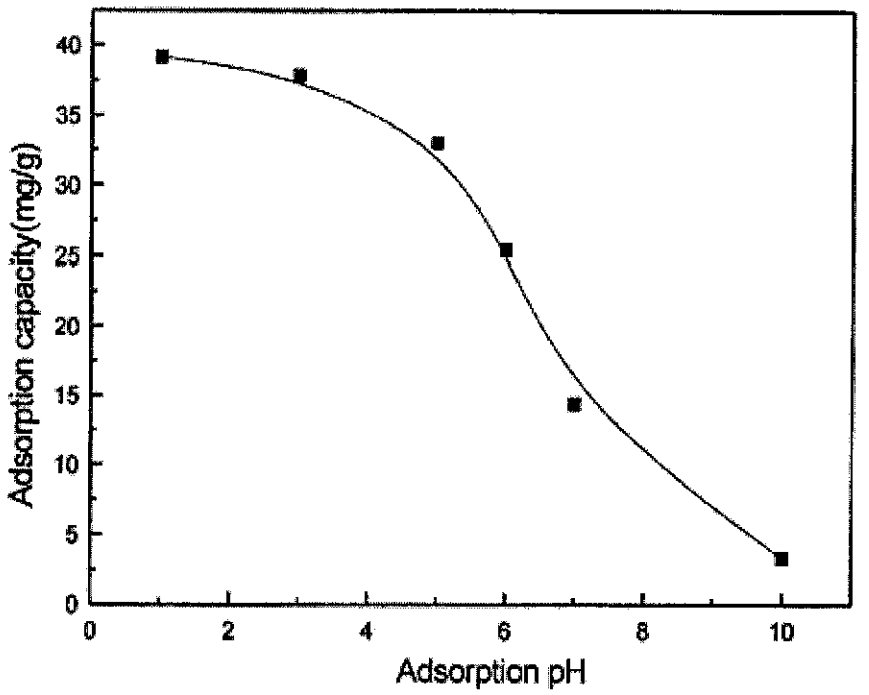

Figure 2.3: Adsorption of Cr (VI) on rice husk based activated carbon as a function of pH. Conditions—contact time: 2 h; RHC: 0.8 g l−1; Cr (VI): 39.51 mg l−1; temperature: 20 ◦C [3].

A graph shown above is an example on the effect of pH to the adsorption activities. The type of metal adsorped is also one of the factors that may affect the adsorption capacity. At low pH (1-3), the overall surface charge on the particles becomes positives and hinds the approach of positively charged metal cations [8]. The overall surface charge depends on to the surface characteristic of the adsorbents which is affected by the types of activation used [6]. At high pH (7-8), the number of negatively charged groups on the adsorbent matrix probably increases, and enhances the removal of cationic species [8]. The pH value that could be the best condition for the adsorption of metal cations is pH 5.0 [3, 4, 8]. However, the optimum condition for the pH of the adsorption medium does depends on the metal cations that are being adsorp as reported by Horsfall and Ayebaemi et. al (2004) [6].

CHAPTER 3

METHODOLOGY/PROJECT WORK

The methodology of this project can be divided into 2 parts. The first part is the treatment of the rice husk and the second part is the adsorption process.

3.1 TREATMENT OF THE RICE HUSK

1. About 300 g of raw rice husk was washed with distilled water several times to remove the dirt in the rice husk collected.
2. The washed rice husk was then dried in an oven at 100°C for 24 hrs.
3. Dried rice husk was grinded and sieved through 500 μm, 250 μm, 125 μm and 100 μm sieve tray. The rice husk of size between 250 μm to 500 μm was chosen to be digested.
4. 5 g of raw rice husk was digested with 100 ml of 1.0 M nitric acid and 100 ml of 1.0 M sodium hydroxide for a time varying from 3 hrs to 15 hrs. They were labeled as DH3, DH6, DH9 and DH15 respectively.
5. The digested rice husk was filtered and washed with excess distilled water until the filtrate was free from acid and again dried in an oven at 120°C for 2 hrs.
6. The rice husk then was pyrolized in a furnace in air at 500°C for 1 hr.

3.1.1 Preparation of 1.0 M of Nitric Acid

1. 69.24 ml of nitric acid (65% by volume) was diluted with distilled water in a 1 L volumetric flask.

3.1.2 Preparation of 1.0 M Sodium Hydroxide

1. 40.00 grams of solid sodium hydroxide was dissolved with distilled water in 1 L volumetric flask.

3.1.3 Preparation of 20 ppm, 40 ppm, 60 ppm and 100 ppm of $ZnCl_2$

1. 40 ml of 500 ppm Zn^{2+} was poured in 1 L of volumetric flask and it was then filled in 1 L of distilled water until it reaches the 1 L mark on the volumetric flask.
2. Step 1 was repeated for 40 ppm, 60 ppm and 100 ppm of Zn^{2+}.
   (Refer to 3.5.3 for calculation)

3.2 EFFECT OF DIGESTION TIMES ON BASIC AND ACIDIC ACTIVATION ON ADSOPRTION ACTIVITIES

1. 25 ml of 30 ppm $ZnCl_2$ was mixed with 0.1 g pyrolised rice husk from DH3 of acidic activation. The same procedure applied for rice husk from DH3 of basic activation.
2. Then, both solutions were left for 90 minutes.
3. Each solution was then filtered and the residual was analyzed using AAS (Absorption Atomic Spectrophotometer) to study the concentration of Zn^{2+} left in the residual.
4. Step 1 to 4 was repeated for DH6, DH9 and DH15 of the pyrolised rice husk.
5. A graph of percent metal uptake vs. digestion times was plotted for rice husk with different activation chemical in the same graph.
6. A graph of adsorption capacity vs. digestion times was plotted for rice husk with different activation chemical in the same graph.

3.3 EFFECT OF CONTACT TIME ON ADSORPTION ACTIVITIES

1. 25 ml of 40 ppm $ZnCl_2$ was mixed with 0.1 g pyrolised rice husk from DH15 of acidic activation. The same procedure applied for rice husk from DH15 of basic activation.
2. Then, both solutions were left for 15 minutes.
3. The solution was then filtered and the residual was analyzed using AAS (Absorption Atomic Spectrophotometer) to study the concentration of Zn^{2+} left in the residual.
4. Step 1 to 4 was repeated for 30, 45, 60, 75 and 90 minutes of the contact time.

5. A graph of percent metal uptake vs. contact time was plotted for rice husk with different activation chemical in the same graph.
6. A graph of adsorption capacity vs. contact time was plotted for rice husk with different activation chemical in the same graph.

3.4 EFFECT OF INITIAL METAL CONCENTRATION ON ADSORPTION ACTIVITIES

1. 25 ml of 20 ppm $ZnCl_2$ was mixed with 0.1 g pyrolised rice husk from DH15 of acidic activation. The same procedure applied for rice husk from DH15 of basic activation.
2. Then, both solutions were left for 90 minutes.
3. Each solution was then filtered and the residual was analyzed using AAS (Absorption Atomic Spectrophotometer) to study the concentration of Zn^{2+} left in the residual.
4. Step 1 to 4 was repeated for 40 ppm, 60 ppm and 80 ppm $ZnCl_2$.
5. A graph of percent metal uptake vs. initial metal concentration was plotted for rice husk with different activation chemical in the same graph.
6. A graph of adsorption capacity vs. initial metal concentration was plotted for rice husk with different activation chemical in the same graph.

3.5 CALCULATION

3.5.1 Calculation of Dilution of Nitric Acid (65% by volume) to make 1 L of 1.0M Nitric Acid

1. Required Nitric Acid = 1 L of 1.0 M Nitric Acid

V_{total} = 2.5 L

$$V_{acid} = \frac{65}{100} \times 2.5 L$$

= 1.625 L acid

$$\text{Mass of acid} = 1.625 L \times \frac{1.4 g}{ml} \times \frac{1000 ml}{1 L}$$

= 2275 g

$$\text{Moles of acid} = 2275\,g \times \frac{1\,mol\,acid}{63.01\,g\,acid}$$

$$= 36.105 \text{ g}$$

$$\text{Concentration of acid} = \frac{36.105\,g\,acid}{2.5\,L\,solution}$$

$$= 14.442 \text{ M acid}$$

$M_1V_1 = M_2V_2$

$(14.442)\ (V_1) = (1.0)\ (1\ L)$

$$V_1 = \frac{1}{14.442}$$

$= 0.06924$ L

= 69.24 mL of Nitric Acid (65% by volume)

3.5.2 Calculation to make 1 L of 1.0 M Sodium Hydroxide

1. Required Sodium Hydroxide = 1 L of 1.0M Sodium Hydroxide

$$\text{No. of moles Sodium Hydroxide} = \frac{MV}{1000}$$

$$n = \frac{1(1\,L)}{1\,L}$$

n = 1 moles of NaOH

$$\text{Molecular weight of NaOH} = \frac{40.0\,g\,NaOH}{Mol\,of\,NaOH}$$

$$\text{Mass of NaOH required} = \frac{40.0\,g\,NaOH}{Mol\,of\,NaOH} \times 1\,mol\,NaOH$$

= 40.0 g of NaOH

3.5.3 Calculation of 20 ppm, 40 ppm, 60 ppm, and 100 ppm of $ZnCl_2$

1. To minimize error, the solution prepared was started from 500 ppm $ZnCl_2$

$$500 \text{ ppm by mass} = \frac{500\,mg\,Zn^{2+}}{1\,kg\,of\,water}$$

Assuming 1.0 mol of $ZnCl_2$, thus having 1.0 mol of Zn^{2+}

$$\text{Mass of ion Zn2+} = \frac{65.39\,g\,Zn^{2+}}{1\,mol\,of\,Zn^{2+}} \times 1\,mol\,of\,Zn^{2+}$$

$$= 65.39 \text{ g of } Zn^{2+}$$

$$\text{Mass of } ZnCl_2 = \frac{136.28\,g\,ZnCl_2}{1\,mol\,of\,ZnCl_2} \times 1\,mol\,of\,ZnCl_2$$

$$= 136.28 \text{ g } ZnCl_2$$

$$\text{Percent mass of ion Zn2+} = \frac{65.39\,g\,Zn^{2+}}{136.28\,g\,ZnCl_2}$$

$$= \frac{0.4798\,g\,Zn^{2+}}{1.000\,g\,ZnCl_2}$$

Therefore to get 500 mg of Zn^{2+} in $ZnCl_2$

$$0.5\,g\,of\,Zn^{2+} \times \frac{1.000\,g\,ZnCl_2}{0.4798\,g\,Zn^{2+}}$$

= 1.042 g of $ZnCl_2$

To prepare 20 ppm Zn^{2+}

$M_1V_1 = M_2V_2$

$500V_1 = 20(1)$

$$V_1 = \frac{20}{50}$$

$= 0.04$ L $= 40$ mL

To prepare 40 ppm Zn^{2+}

$M_1V_1 = M_2V_2$

$500V_1 = 40(1)$

$$V_1 = \frac{40}{50}$$

$= 0.08$ L $= 80$ mL

To prepare 60 ppm Zn^{2+}

$M_1V_1 = M_2V_2$

$500V_1 = 60(1)$

$$V_1 = \frac{60}{50}$$

$$= 0.12 \text{ L} = 120 \text{ mL}$$

To prepare 80 ppm Zn^{2+}

$M_1V_1 = M_2V_2$

$500V_1 = 80(1)$

$$V_1 = \frac{80}{50}$$

$$= 0.16 \text{ L} = 160 \text{ mL}$$

3.5.4 Percent Metal Uptake

The calculation for percent metal uptake is as below:

$$\frac{Initial\ Concentration - Final\ Concentration}{Initial\ Concentration} \times 100\% = \text{Percent Metal Uptake}$$

Let say the initial concentration are 40 ppm and the final concentration are 20 ppm, therefore the percent metal uptake is

$$\frac{40\ ppm - 20\ ppm}{40\ ppm} \times 100\% = 50\% \text{ metal uptake}$$

3.5.5 Adsorption Capacity

The calculation for adsorption capacity is as below;

$$\frac{Initial\ Concentration - Final\ Concentration}{Weight\ of\ rice\ husk\ in\ gram} \times volume\ of\ solution\ in\ L$$

Let say the initial concentration is 40 ppm and the final concentration is 20 ppm, volume of solution 0.025 L and the weight of rice husk used is 0.1 gram, therefore the adsorption capacity is

$$\frac{40\ ppm - 20\ ppm}{0.1\ g\ rice\ husk} \times 0.025\ L = 5\ mg\ Zn(II)/g\ rice\ husk$$

3.6 ATOMIC ABSORPTION SPECTROSCOPY (AAS) METHOD

Atomic absorption spectroscopy (AAS) is the appropriate term used when electro-magnetic radiation (EMR) is absorbed or emitted by atoms and measured. All atoms can absorb EMR, and the wavelengths at which EMR is absorbed or emitted is exclusive for a particular chemical element. AAS is a quantitative method to analyze the concentration of many metals. Thus, in this experiment AAS is used to analyze the quantity of the Zn (II) content in the solution.

In order to use the AAS, the first step is the preparation of the standard solution of Zn (II) solution. The rule of thumb that should be followed to analyze the Zn (II) content is to ensure that the range of standard solution must be bigger then the range of the expected outcome of the Zn (II) content.

After the standard solution has been prepared, together with the samples, they were analyzed using the AAS. For each standard solution prepared, it represented a particular value for the EMR. For instance, standard solution of 20 ppm Zn (II) gave a value for EMR absorption of 1.2323 whereas for 40 ppm standard solution of Zn (II) gave a value of EMR absorption of 1.3435.

After completing the analysis for standard solution, a graph of absorption against concentration was plotted by the AAS. Thus, by analyzing the absorption for each sample, the concentration of metal ion in each sample could be determined. Therefore, the preparation for the standard solution is very important since it will determine the outcome of the analysis.

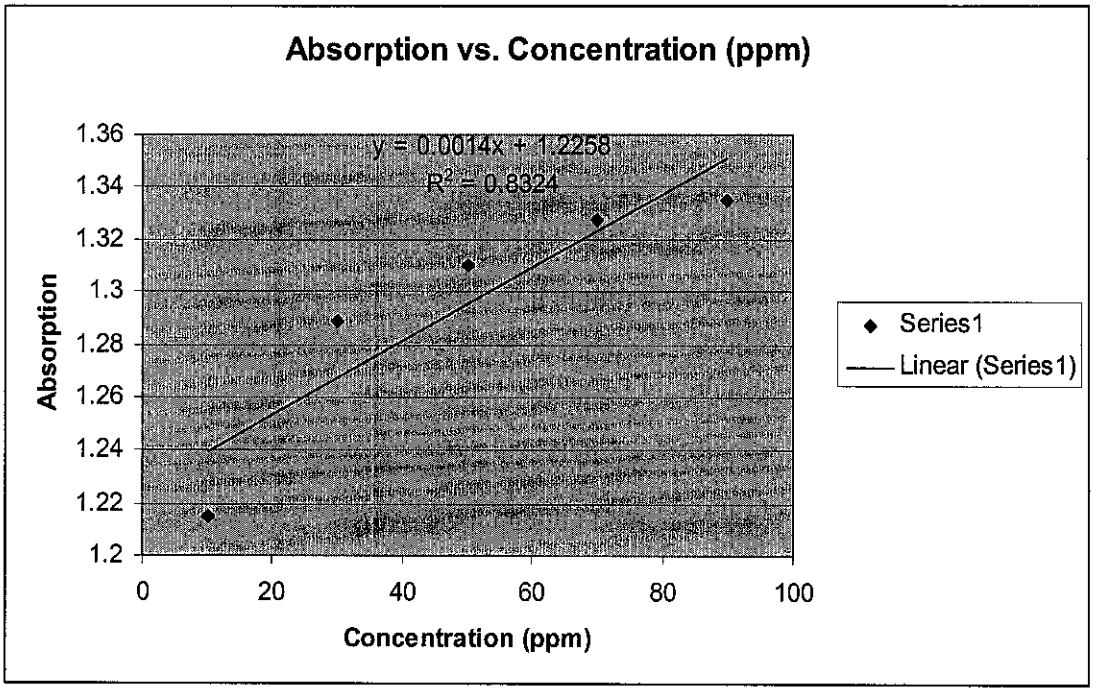

Figure 3.1: Graph of Absorption versus Concentration

A graph shown above is an example of the calibration curve of the AAS. The equation shows can be used to calculate the concentration at the absorption value given. However the value R^2 is 0.8324 indicates that the standard solution given is not carefully prepared. The value of R^2 represents the deviation of the data point collected compare to the straight line graph plotted. The graph in figure 3.1 may promote consistent error to the value of the concentration analyzed. Therefore, it is recommended to prepare another data for the standard solution which have lower value of R^2.

Below are the materials and equipment used for the experiment;

Table 3.1: Chemicals or Materials Required

No.	Chemicals/Materials	Quantity (Volume, mass etc.)	Source
1	Nitric Acid	As per requirement	Chemical Laboratory
2	Sodium Hydroxide	As per requirement	Chemical Laboratory
3	Zinc Chloride	As per requirement	Chemical Laboratory

Table 3.2: Tools/Equipment/Software Required

No.	Equipments	Quantity (Volume, mass etc.)	Source
1	AAS	As per requirement	Chemical Laboratory
2	pH meter	As per requirement	Chemical Laboratory
3	Sieving Machine	As per requirement	Chemical Laboratory

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 PRE-ADSORPTION

Table 4.1: Observations and Weight Samples of The Treated Rice Husk

Types of Activation	Digestion Time		Observations		Weight of sample before digestion (g)	Weight of sample after pyrolization (g)
	Source code	hr	While and After digestion	After pyrolization		
HNO_3	DH3	3	-The solution colour is light brown. - non sticky and sandy	The sample colour is dark black.	5.0	1.1
	DH6	6	-The solution colour is light brown. - non sticky and sandy	The sample colour is dark black.	5.0	0.9
	DH9	9	-The solution colour is light brown. - non sticky and sandy	The sample colour is dark black.	5.0	Not completed
	DH15	15	-The solution colour is light brown. - non sticky and sandy	The sample colour is dark black.	5.0	1.3

Types of Activation	Digestion Time		Observations		Weight of sample before digestion	Weight of sample after pyrolization
	Source code	hr	While and After digestion	After pyrolization		
NaOH	DH3	3	-The solution colour is dark yellow. - sticky and slippery	The sample colour is grey black.	5.0	0.6
	DH6	6	-The solution colour is dark yellow. - sticky and slippery	The sample colour is grey black.	5.0	0.5
	DH9	9	-The solution colour is dark yellow. -sticky and slippery	The sample colour is grey black.	5.0	Not completed
	DH15	15	-The solution colour is dark yellow. -sticky and slippery	The sample colour is grey black.	5.0	0.8

As the sample was mixed with acidic solution, the mixture colour turned into light brown from colourless and the filtrate was non sticky and sandy. After pyrolisation, the sample colour turned into dark black from light brown.

As the sample was mixed with basic solution, the mixture colour turned into dark yellow from colourless and the filtrate was sticky. After pyrolisation, the sample colour turned into grey black from dark yellow.

The observation showed that the weight of the sample decreased for both activations. However, there was no trend shown for both type of activation. The pyrolisation process was performed in order to increase the rice husk surface area. The reduction in weight of the rice husk could be due to the lost due to air flow. It was noticed that after the pyrolisation process, the samples treated with basic solution showed greater reduction in weight compared to the ones treated with acidic solution.

4.2 ADSORPTION

4.2.1 Effect of Digestion Time of Basic and Acidic Activation on Adsorption Activities

Table 4.2: Final Concentration of Zn (II) concentration in ppm (Digestion Times)

Digestion Time (hr)	Basic Activation (NaOH) (ppm)	Acidic Activation (HNO_3) (ppm)
3	25.01	20.85
6	23.21	12.85
9	20.25	5.66
15	17.33	0.00

Table 4.3: Percent Metal Uptake (Digestion Times)

Digestion Time (hr)	Basic Activation (NaOH) (ppm)	Acidic Activation (HNO_3) (ppm)
3	16.63	30.5
6	22.63	57.17
9	32.5	81.13
15	42.23	100.00

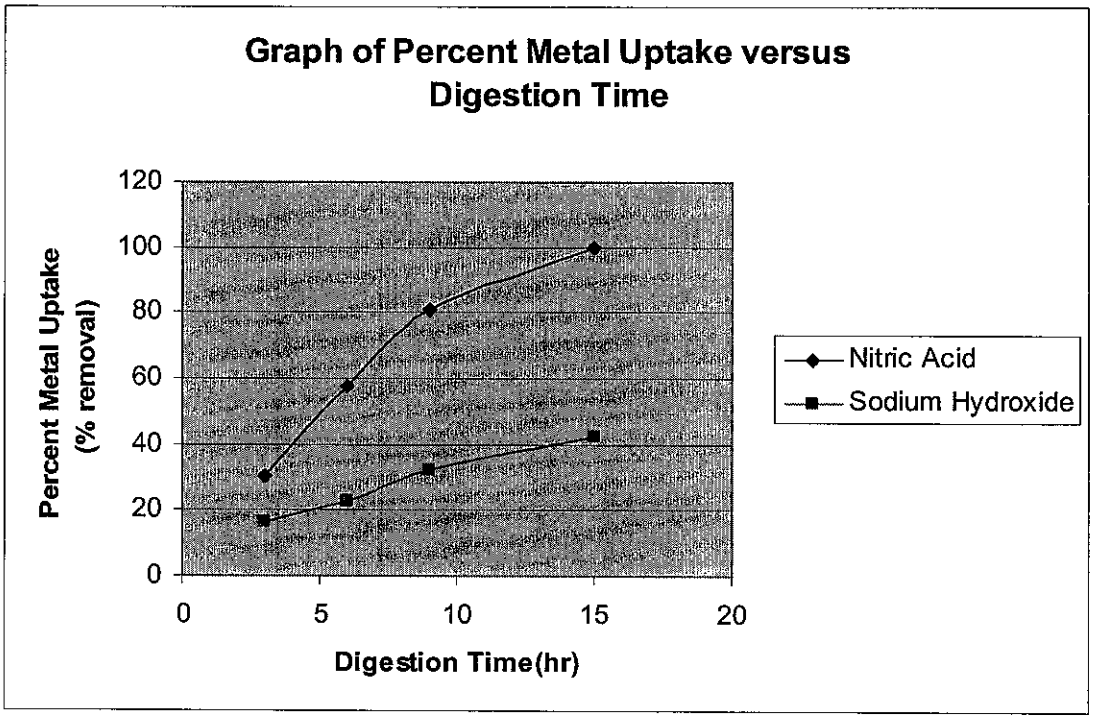

Figure 4.1: Graph of percent metal uptake versus digestion time

From the graph shown above, it was found that percent metal uptake increased with the increasing of digestion time. It was also observed that the activation using acidic solution was better compared to the activation using basic solution. The results of this experiment support the finding by Horsfall and Ayebaemi et. al (2004) on the biomass activation using acidic and basic solution [6]. It is believed that activation using the acidic solution would have enhanced the surface property of the rice husk better than the basic solution [6]. Adsorption being a surface phenomenon, the smaller adsorption sizes offered comparatively larger surface area and hence higher adsorption occurs at equilibrium [4].

Table 4.4: Adsorption Capacity (mg Zn (II) / g rice husk)

(Digestion Times)

Digestion Time (hr)	Adsorption Capacity (mg Zn (II) / g rice husk)	
	Basic Activation ($NaOH$)	Acidic Activation (HNO_3)
3	1.25	5.11
6	1.70	5.85
9	2.44	6.29
15	3.17	7.50

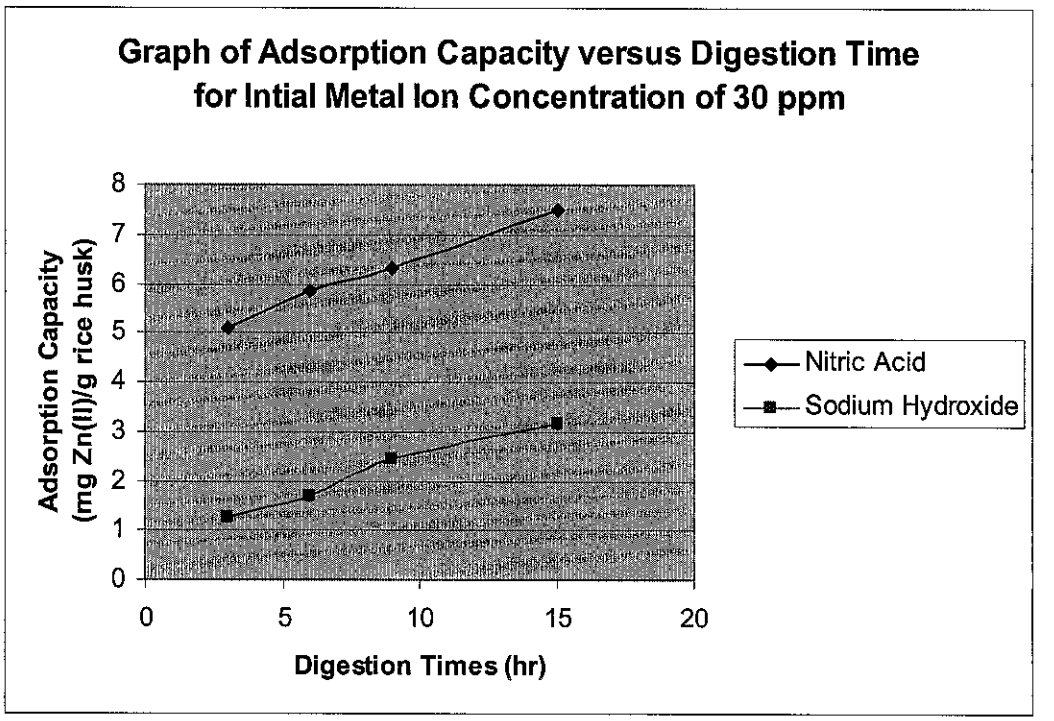

Figure 4.2: Graph of adsorption capacity versus digestion time for initial metal ion concentration of 30 ppm

Adsorption capacity of the adsorbent means the amount of adsorbate that can be adsorped per grams of adsorbent. In this piece of work, it refers to how much Zn (II) ion can be adsorped per grams of rice husk. From the graph shown in figure 4.2, it was noted the adsorption capacity of the rice husk increased as the digestion time increased. Scanning Electron Micrographs of the digested rice husk showed that the size of the rice husk has decreased with the increasing time of digestion [1]. Further investigation also noted that the extent of the porosity of the individual particle was increased [1]. According to Rahman, Ismail and Osman et. al (2000), the longer

digestion time has created the larger internal surface area or a maximum porous structure.

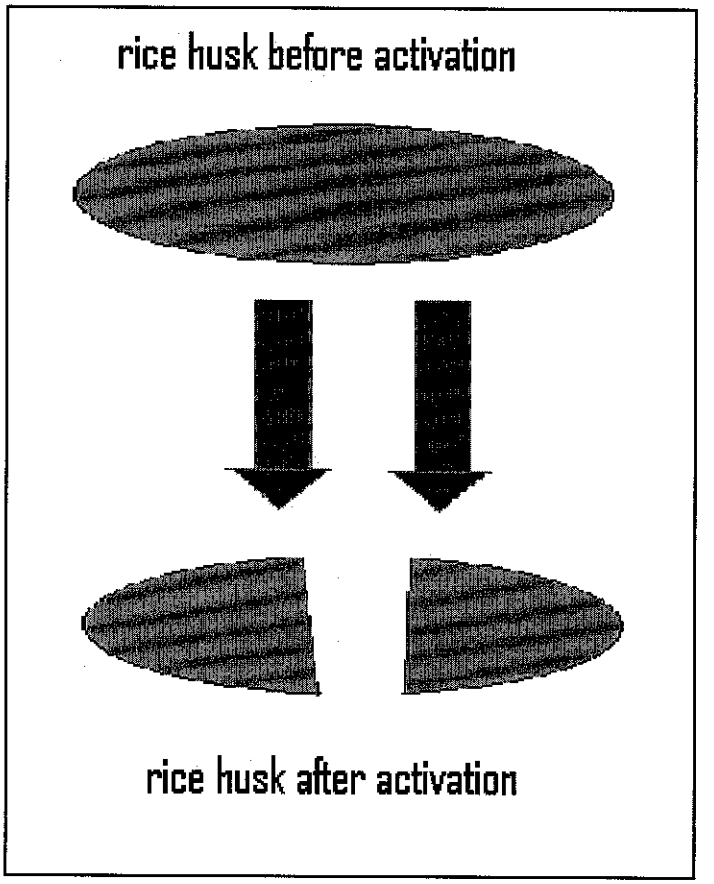

Figure 4.3: Surface Property Enhancement

Figure 4.3 shows a simple way of explaining the surface property enhancement of the rice husk. Before the activation, there is no internal surface area in between the crack as compared after the activation. Thus, the internal surface area has increase after the activation process occur [1]. In real case, the rice husk may have been cracked in so many small portions which promote a better enlargement of the internal surface area.

4.2.2 Effect of Contact Time on Adsorption Activities

Table 4.5: Final Concentration of Zn (II) concentration in ppm (Contact Time)

Contact Time (minutes)	Basic Activation (NaOH) (ppm)	Acidic Activation (HNO_3) (ppm)
15	31.8157	28.3839
30	24.1896	20.0788
45	18.4967	13.4789
60	14.9706	5.4889
75	10.5805	0.0289
90	9.5559	0.0000

Table 4.6: Percent Metal Uptake (Contact Time)

Contact Time (minutes)	Basic Activation (NaOH) (ppm)	Acidic Activation (HNO_3) (ppm)
15	20.46	29.04
30	39.53	49.8
45	53.76	66.3
60	62.57	86.28
75	73.55	99.93
90	76.11	100

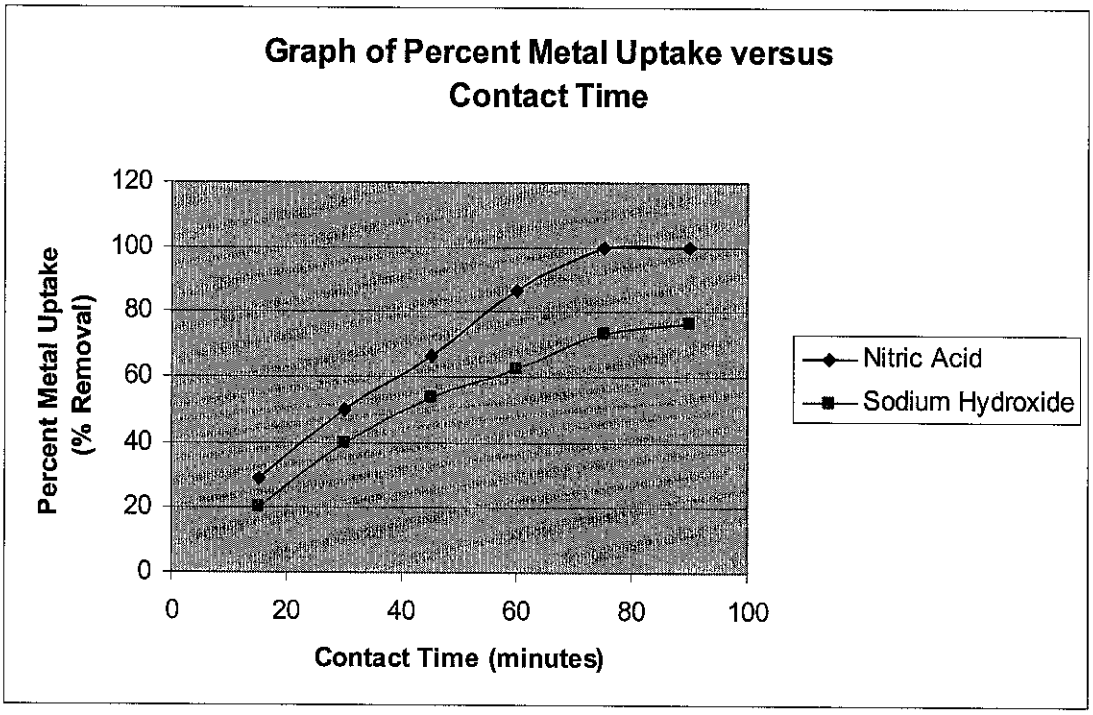

Figure 4.4: Graph of percent metal uptake versus contact time

From the graph shown in figure 4.4, percent metal uptake increased with the increasing of contact time until the system reached equilibrium. This phenomenon was indicated at contact time of 75 minutes for the acid treated rice husk and 90 minutes for the base treated rice husk. A fast kinetics is one of the most important aspects for adsorption process [8]. It was reported by Montanher, Oliveira and Rollemberg (2005) that contact time of 10 minutes was sufficient to achieve equilibrium for adsorption of Zn (II) ion by rice husk. However, the contact time depends on the analytical speed and removal efficiency. The difference in contact time as reported by Montanher, Oliveira and Rollemberg (2005) could be due to the usage of stirrer while the adsorption process was performed.

Table 4.7: Adsorption Capacity (mg Zn (II) / g rice husk)

(Contact Time)

Contact Time (minutes)	Adsorption Capacity (mg Zn (II) / g rice husk)	
	Basic Activation (NaOH)	Acidic Activation (HNO_3)
15	2.05	2.90
30	3.95	4.98
45	5.38	6.63
60	6.26	8.63
75	7.35	9.99
90	7.66	10.00

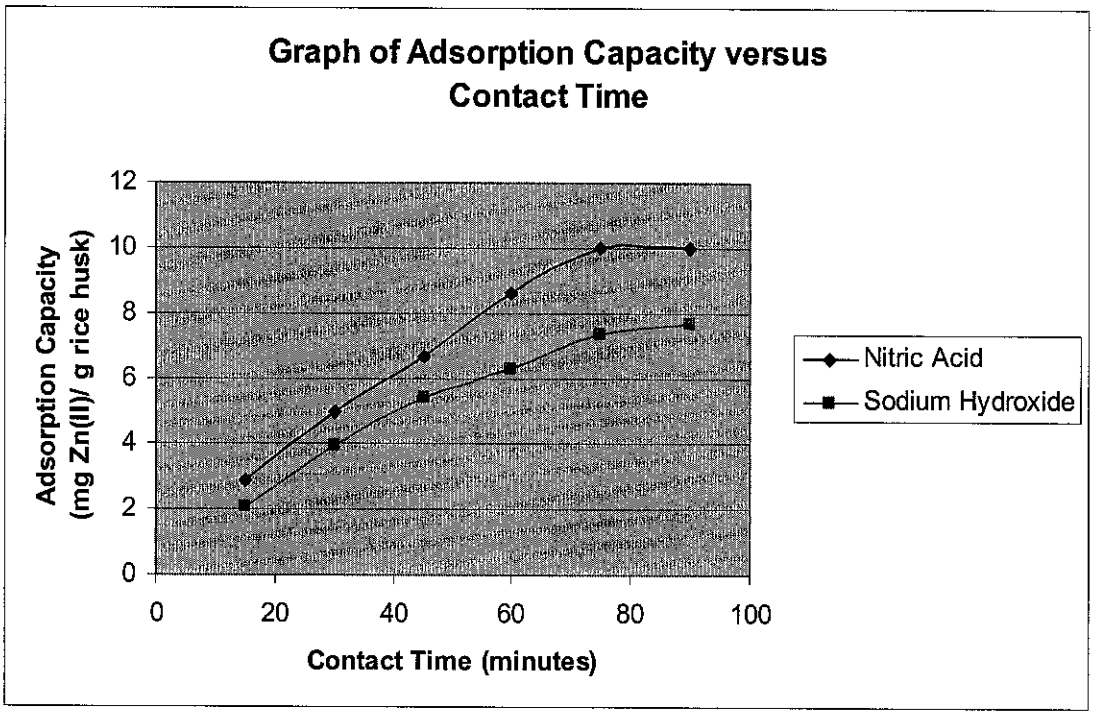

Figure 4.5: Graph of adsorption capacity versus contact time

As shown in figure 4.5, it was found that the adsorption capacity of the rice husk increased as the contact time increased. This indicates that the adsorption process has reached equilibrium. Further action taken to increase the contact time after saturation has been reached will not change the adsorption capacity of the rice husk.

4.2.3 Effect of Initial Metal Ion Concentration on Adsorption Activities

Table 4.8: Final Concentration of Zn (II) concentration in ppm (Initial Metal Ion Concentration)

Initial Metal Ion Concentration (ppm)	Basic Activation (NaOH) (ppm)	Acidic Activation (HNO_3) (ppm)
20	0.00	0.00
40	9.55	0.00
60	42.16	30.14
80	70.78	61.51

Table 4.9: Percent Metal Uptake (Initial Metal Ion Concentration)

Initial Metal Ion Concentration (ppm)	Basic Activation (NaOH) (ppm)	Acidic Activation (HNO_3) (ppm)
20	100.00	100.00
40	76.11	100.00
60	29.73	49.77
80	11.52	23.11

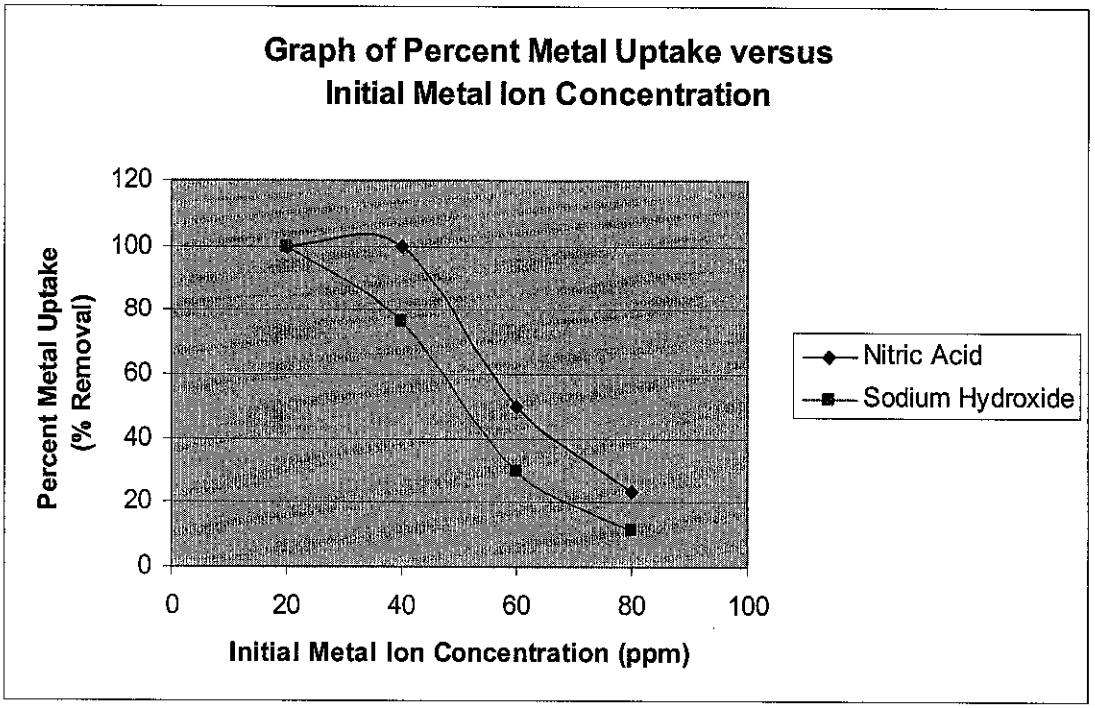

Figure 4.6: Graph of percent metal uptake versus initial metal ion concentration

From figure 4.6, it was observed that percent metal uptake decreased with the increasing initial metal ion concentration. This indicates that the adsorption rate becomes much more ineffective as the initial metal concentration is increased. Also, it was noted that the acid treated rice husk have the same value of percent metal uptake for initial metal concentration of 20 ppm and 40 ppm of Zn (II) ion. This phenomenon was further explained referring to figure 4.7.

As the initial metal ion concentration increased, the initial metal ion loading also increased. This phenomenon causes an equal increase in number of Zn (II) ions coming in contact with rice husk increases during same interval of time while on the other hand the numbers of adsorbing sites available for adsorption are constant for all concentrations. So when influent concentration is higher, more number of ions will be competing for same the adsorption sites and will go through without being adsorped [5].

Table 4.10: Adsorption Capacity (mg Zn (II) / g rice husk)
(Initial Metal Ion Concentration)

Initial Metal Ion Concentration (ppm)	Adsorption Capacity (mg Zn (II) / g rice husk)	
	Basic Activation (NaOH)	Acidic Activation (HNO_3)
20	5.00	5.00
40	7.61	10.00
60	4.46	7.46
80	2.30	4.62

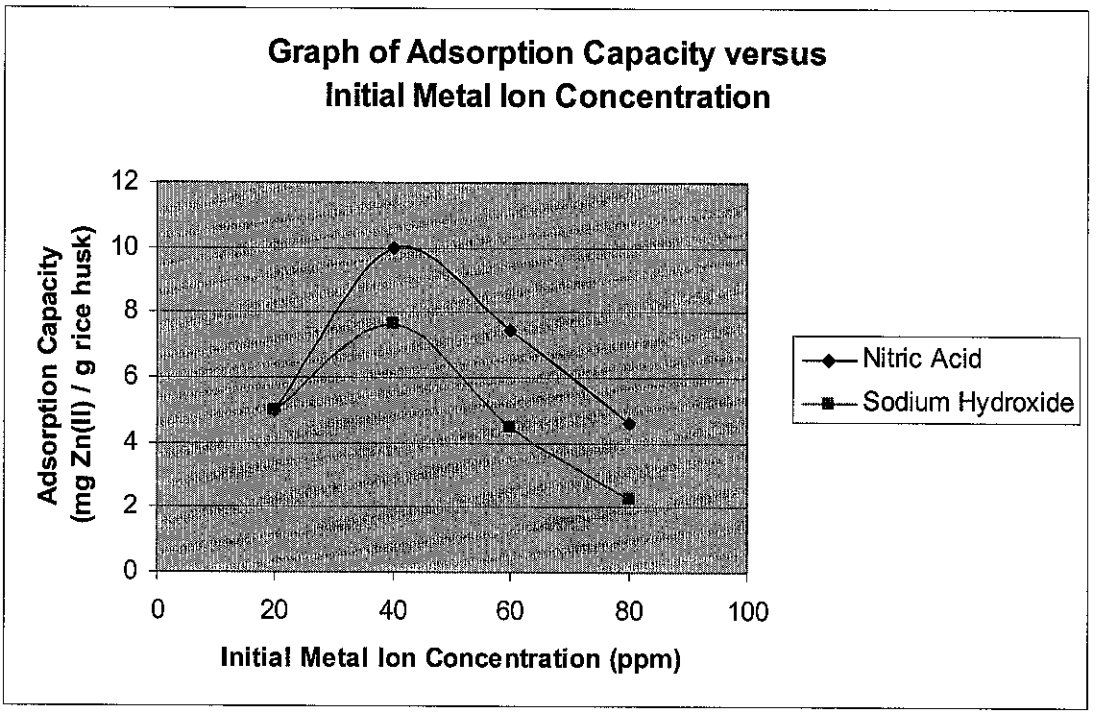

Figure 4.7: Graph of adsorption capacity versus initial metal ion concentration

From graph shown above, the optimum condition for maximum Zn (II) ion adsorption to occur is at initial metal ion concentration of 40 ppm. Also, it was observed that the adsorption capacity increase as the initial metal ion concentration increased until an optimum condition was reached. Then, the adsorption gradually started to decrease. At low initial metal ion concentration (20 ppm to 40 ppm), the adsorbate could occupy the active sites on the rice husk surface efficiently [3]. In other words, the ratio of surface active sites to total metal is high and hence all metal may interact with the rice husk and be removed from the solution [8]. However, at high metal concentration (40 ppm to 80 ppm), the adsorption efficiency was reduced with increasing initial metal ion concentration in the solution thus indicating saturation [8].

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 CONCLUSION

Based on the results obtained, the conclusions that can be made are as follows:

1) As the digestion time increases, the Zn (II) ion adsorped will also increases. Acid treated rice husk showed better performance as an adsorbent compared to base treated rice husk.
2) As the contact time increases, the Zn (II) ion adsorped will also increase until saturation is reached.
3) As the initial metal concentration is increase, the Zn (II) ion adsorped also increase until the concentration is 40 ppm. Further increase in the initial metal concentration ion will result in the decrease of Zn (II) ion adsorped.

5.2 RECOMMENDATIONS

1) To study surface area of the samples using BET method. By obtaining the sample surface area, the relation between adsorption of the Zn (II) ion by the rice husk and the surface properties can be justified.
2) To study the sample porosity by using the Scanning Electron Microscope (SEM) and relate the results obtained with the findings in this piece of work.
3) To collect more supporting data that may help to strengthen the observation that has been made i.e. additional data for effect of contact time.

CHAPTER 6

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